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A new method for measuring RBA applied to the Page equation for the tensile strength of paper.

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Abstract

The Page equation is the most widely used equation to predict the tensile strength of paper. In this paper, the derivation of the Page equation is examined critically and a modified Page equation is proposed based on a newly developed method to calculate the relative bonded area from sheet density and fibre shape. The predictions of the original and modified Page equations were then tested against twelve sets of sheets made from different unbleached, never dried radiata pine kraft pulps. The bond strength was used as a fitting parameter. The best fit bond strengths varied so widely as to make it impossible to use either the original or modified Page equation to predict tensile strength, without prior knowledge of the bond strength applicable to that data set.

Introduction

Paper is a complex network of fibres that are bonded together through hydrogen bonds at points where fibres cross each other. Every paper grade needs at least some strength to satisfy both the converting operation and the end use of the product. Tensile strength is the most commonly used parameter for describing the mechanical properties of a sheet of paper.

There have been several analytical models for the paper strength, that are discussed and compared in *(1)*. They have differences in approach but all assume that the strength of paper is determined by the strength of the individual fibres and the strength of bonding of the fibres into the network. The most commonly used analytical equation for the strength of paper is the Page equation *(2)*.

The Page equation is based on two important assumptions. The first assumption is that during the straining process the load is taken by progressively fewer fibres crossing the rupture line. The paper will break catastrophically when the fibres lying in the direction of the loading reach their rupture strain. This implies that the fibres across the failure line can be divided into two fractions. One fraction (n_f) is composed of fibres that take the load at failure and then break, the other fraction (n_p) consists of fibres that pull out intact due to prior bond breakage. Page assumed that these fibres carry no load at paper failure. Under these assumptions, in combination with the relationship between finite-span tensile strength, T (kNm/kg), and zero span tensile strength, Z, (kNm/kg) and the Cox *(3)* result of a Poisson's ratio of one third for isotropic (random) sheets, Page was able to write

$$T = 8n_f Z / 9(n_f + n_p) \qquad 1$$

The second assumption was that the number of fibres pulled out to the number of fibres broken is only dependent on the ratio of fibre strength, ϕ, and bond strength, β, i.e. $n_f / n_p = f(\phi/\beta)$. The simplest form of the function, $n_f / n_p = \phi/\beta$, was chosen by Page, i.e.

$$\frac{1}{T} = \frac{9}{8}\left[\frac{1}{Z} + \frac{1}{Z}\frac{\phi}{\beta}\right] \qquad 2$$

The fibre strength was related to the zero-span strength by *(4)*,

$$\phi = (8/3)AZ \qquad 3$$

where A is the fibre cross-sectional area. This form has been modified from that originally used by Page so as to express fibre strength in Pa rather than breaking length. The bond strength was assumed to be given by

$$\beta = bP\frac{L}{4}RBA \qquad 4$$

where b is the shear bond strength in Pascals, P is the fibre perimeter (m), L is the fibre length and RBA is the relative bonded area- i.e. the fraction of the fibre surface that is bonded to other fibres.

The assumptions underlying equation 4 need to be considered carefully. The factor of $L/4$ arises from the fact that a fracture line will divide a fibre into two segments of unequal length and the length of the shortest segment will be randomly and equally distributed along a half fibre length giving an average length of $L/4$. The factor $bP\ RBA$ then assumes that bonding takes place around the whole perimeter of the fibre and that that the bond acts collectively, i.e. that all of the fibre crossings that create the bonded area can be treated as if they are one bond with total area $PL/4RBA$ and bond strength, b. This is unrealistic. Direct experimental measurements *(5)* and theory *(6, 7)* show that stress is transferred into a fibre of interest by a shear-lag mechanism in which the bonds at the end of the fibre are most heavily loaded. The concept of the bonds acting collectively, i.e. that all of the bonds are equally loaded is therefore not correct. The implications of this will be discussed further in this report.

Substituting equations 3 and 4 in equation 2 then yields the Page equation *(2)* as

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho_w}{bPL(RBA)} \qquad 5$$

where Z is the zero span tensile index (*kNm/kg*), A is the average fibre cross section area (m^2), ρ_w is the density of the fibre (kg/m^3), P is the perimeter of the fibre cross section (m), L is the length of the fibre (m) and *RBA* is the relative bonded area.

Modification of Page equation

To test the predictions of the Page equation it is necessary to measure all variables for a given sheet. Measurements of zero-span strength and fibre length are relatively straightforward. Coarseness can also be measured using an automated fibre analyser, providing the measurements are done carefully. The measurement of fibre perimeter is considerably harder as no automated instrument is available to measure perimeter. Available methods include using a confocal microscope, either on single fibres *(8)* or on sheet cross-sections *(9)* or by using a conventional microscope on oriented fibres *(10)*. The measurement of bond strength is very difficult. A variety of different methods have been tried to prepare joints for testing and measured values have ranged from 2.0 MPa *(11)* to 30 MPa *(12)*. This conference also contains a report of a method to infer the bond strength from measurements on the sheet *(13)* by using HCl gas exposure to weaken the fibres until the fibres crossing the failure line all break. The estimated shear bond strength for sheets from a 60% yield radiata pine kraft pulp was 26.9 MPa.

Up until recently, the measurement of RBA would have been considered to be relatively straightforward. The relative bonded Area is the fraction of the total available fibre surface that is bonded and is defined as $RBA = (A_t - A)/A_t$ where A_t is the total area available for bonding and A is the unbonded area in the sheet after it has been formed. The most commonly used method of measuring *RBA* is the light scattering method *(14)* that assumes that $S = cA_s$, where S is the light scattering coefficient of a sheet, c is a constant that depends both on wavelength and fibre properties and A_s is the surface area available for scattering. If S_0 is the scattering coefficient for a completely unbonded sheet, then $RBA = (S_0 - S)/S_0$.

The major difficulty with the technique is in determining S_0, since an unbonded sheet cannot be prepared. The Ingmanson and Thode extrapolation method *(14)* has been widely used to determine S_0. In this method, scattering coefficient is plotted against tensile strength for sheets made from the same pulp, where the sheet strength is varied by refining and/or by wet pressing. The data is extrapolated to determine the y-axis intercept at zero tensile strength, which is assumed to be S_0. Despite criticism of the method *(15)* since inception, it has remained widely used due to the lack of a practical alternative.

The problems of the extrapolation technique for determining S_0 were also recently highlighted with data, from some of the authors of this work, of sheets in which the fibre length was reduced by cutting the wet sheets, before reslushing them and making handsheets *(16)*. This same data set will be analysed as part of the work reported here. The data set shows a sharp decrease in S_0 from 42.2 to 25.5 m^2kg^{-1} as the length weighted fibre length falls from 3.14 to 1.80 mm. The reduction in S_0 is not physically reasonable as the cutting process would create new surfaces not reduce it and is further evidence that this extrapolation to determine S_0 cannot be correct. The extrapolation method is also completely unsuitable for measuring bonding in machine made papers, since a range of sheets with different strengths cannot be obtained.

Recently we have published papers *(17, 18)* showing that S is inversely linearly proportional to apparent sheet density, ρ_a, provided fibre shape is constant. These papers provided a method to correct S and ρ_a for fibre shape and showed that all the data could be fitted by a straight line when the corrected values were plotted against each other *(17)*. This method is called here the shape correction method. The analysis yielded a remarkably simple expression for RBA for sheets made from a single furnish as:

$$RBA = \frac{\rho_a}{f\,\rho_w}(1-r) \qquad 6$$

where f is defined as the fibre fill factor: the ratio of the fibre wall area to the area of a rectangular bounding box surrounding the fibre *(9)* and ρ_w is the fibre wall density, which was taken to be 1500 kg/m^3. The value of (1-*r*) was determined for different data sets of sheets made from radiata pine softwood kraft, eucalypt hardwood kraft and blends and ranged from 0.66 to 0.77. Assuming for the sake of simplicity that (1-*r*)=3/4, we can then modify the Page equation by substituting equation 6 to yield

$$\frac{1}{T} = \frac{9}{8Z} + \frac{16Af\rho_w^2}{bPL\rho_a} \qquad 7$$

A final correction that will be made to the Page equation is to correct the assumption that the fibres are bonded all the way around their perimeter. In fact the fibres are likely to be bonded only across the width of the fibre, D_W. Substituting $2D_W$ for P yields our final *modified* Page equation as

$$\frac{1}{T} = \frac{9}{8Z} + \frac{8Af\rho_w^2}{bD_wL\rho_a} \qquad 8$$

The main advantage of this modified Page equation is that it includes for the first time the sheet apparent density as a predictor of tensile strength, with the predicted tensile strength increasing as apparent density increases, in accord with general experience. The further advantage of this equation is that tensile strength can now be predicted for a sheet made under a single set of conditions- it is not necessary to prepare a range of sheets with different densities, in order to extrapolate to determine S_0.

In the work that follows several sets of data obtained both at the Australian Pulp and Paper Institute (APPI) as well as ensis-Papro will be compared with the predictions of both the original Page equation and our modified Page equation given as Equation 8. Given the wide range of measured values of bond strength, this will be used as a fitting parameter.

Materials and methods

The sheets prepared at ensis-Papro and APPI were made and tested using quite different procedures so these are described separately.

Ensis-Papro sheets

There were six pulps. These are listed in Table 1, together with their basic fibre dimensions.

Table 1 Fibre length and wall area for the Ensis-Papro pulps

Pulp #	Description	Fibre length (mm)	Wall area (μm^2)
1	Radiata pine lab cook	1.90	190
2	Radiata pine lab cook	2.00	193
3	Radiata pine lab cook	2.04	179
4	Commercially produced radiata pulp made from same feed chips as #5 and #6.	2.71	240
5	Radiata pine lab cook	2.88	233
6	Modified radiata pine lab cook	2.84	264

Pulps 1-3 were prepared from different parts of the same tree. Pulps 4-6 were prepared from the same batch of chips. Pulp 4 was commercially pulped and pulps 5 and 6 were laboratory pulped. Pulps 1-3 and 5 were never dried, unbleached radiata pine laboratory produced kraft pulps prepared under the following conditions. For each sample, a minimum of three kraft pulps were prepared from each chip sample to obtain one of kappa 25±2. A range of pulp kappa number was obtained by varying the H-factor at constant alkali charge for cooks of 300g o.d. chips in 2L Stalsvets digesters. Pulping conditions were: 16% effective alkali charge (as Na_2O), 30% sulphidity, 4:1 liquor-to-wood ratio, 90 minutes to a maximum temperature of 170°C. Pulp 6 was also an unbleached never-dried pulp prepared to Kappa 25+/-2 from the chips used in pulp 5 but using a modified cooking process.

All pulps were disintegrated with a propeller stirrer and screened through a 0.25mm-slotted flatbed screen. After dewatering and fluffing, kappa number was determined. One pulp from each set of chips was selected for subsequent fibre and handsheet analysis. Handsheets were prepared from the never dried pulp and evaluated in accordance with Appita standard procedures. The tensile strength of the sheets was varied with PFI mill refining. The load applied during pulp refining with the PFI mill was 3.4 N/mm at 10% stock concentration. In each data set, the sheets with the lowest strength had been refined for 500 PFI revolutions.

Cross-section fibre dimensions of thickness, width, wall area and wall thickness were measured using embedding and image analysis procedures *(10)* on fibres obtained by rewetting the sheets that had been refined to 500 PFI revolutions. Length weighted average fibre lengths were determined with a Kajaani FS 200 instrument using Tappi T271 pm-91.

APPI sheets

These were made from a single starting stock of an unbleached laboratory made never-dried radiata pine kraft pulp, with a kappa number of 30. In addition to the starting stock, different fractions were generated from the starting pulp by either hydrocyclone fractionation or cutting the fibres to reduce their length. A moving belt former was used to make handsheets. Five sets of sheets were made from each fraction, each with a different pressing pressure, so as to adjust the sheet density. The fibre cross-sectional dimensions were measured on the fibres *in-situ* in the sheet cross-sections that were embedded in resin and then exposed by polishing the resin embedded blocks with abrasive paper *(9, 19, 20)*. A confocal microscope was used to image the fibres to avoid artefacts from surface preparation. The fibre lengths were measured with a Kajaani FS200. The fibre length and wall area for the pulps used to make the APPI sheets are shown in Table 2.

Table 2 Fibre dimensions used for APPI test material

Number	Label	Length weighted fibre length (mm)	Fibre wall area (µm2)
7	L0	3.14	203
8	L1	2.53	204
9	L2	2.12	196
10	L3	1.79	196
11	Accepts	3.00	220
12	Rejects	3.34	193

Results

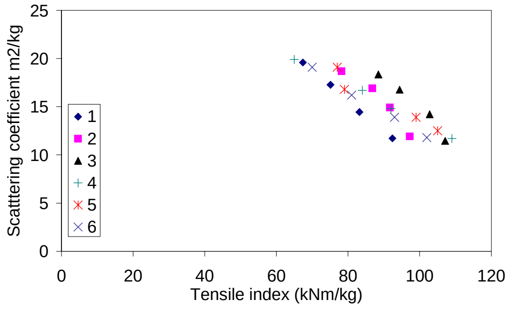

Figure 1 Scattering coefficient versus tensile strength for the Ensis-Papro data.

Figure 1 shows the scattering coefficient as a function of the tensile strength for the Ensis-Papro data. The corresponding figure for the APPI data is shown in Figure 2.

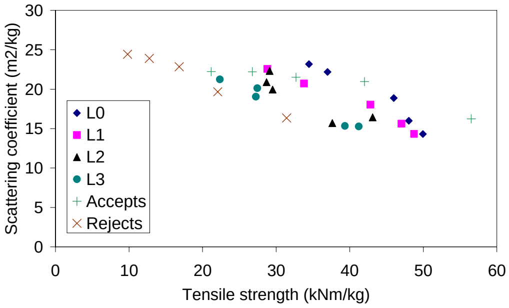

Figure 2 Scattering coefficient versus tensile strength for the APPI data

The fits and R^2 values are shown in for each data set in Table 3.

Table 3 Y-axis intercepts (S_0) and statistics for the linear fits to the data shown in Figure 1 and Figure 2.

Number	Label	S_o	R^2
1	Radiata pine lab cook	41.0	1.00
2	Radiata pine lab cook	46.5	0.95
3	Radiata pine lab cook	50.2	0.97
4	Commercially produced radiata pulp made from same feed chips as #5 and #6.	32.2	1.00
5	Radiata pine lab cook	33.7	0.93
6	Modified radiata pine lab cook	34.6	1.00
7	L0	42.0	0.94

8	L1	34.1	0.98
9	L2	32.3	0.79
10	L3	28.6	0.97
11	Accepts	26.6	0.85
12	Rejects	28.8	0.98

Each of the data sets, except for L3 and the Accepts, has been well fitted with a straight line. However, Figure 1, Figure 2 and Table 3 show the difficulties of this type of extrapolation. The minimum strength of any of the ensis-Papro sheets was 65kNm/kg for pulp no. 4 and the maximum range of tensile strength for any of the ensis-Papro data sets was only 40kNm/kg. Thus the data must be extrapolated over a span of tensile strength at least 1.5 times larger than the span of the actual data. Such extrapolations are problematic, even if it were certain that a straight line provided the best fit to the data. This is by no means certain. The original Ingmanson and Thode paper showed a non-linear relationship between scattering coefficient and tensile strength for weak sheets, with the slope of the curve tending to flatten out and reach a plateau at low strengths. Figure 1 and Figure 2 indirectly support this, since the maximum scattering coefficient measured for any of the sheets was only 24.43 m^2/kg despite S_0 values ranging from 50 to 26 m^2/kg. There is no evidence that the scattering coefficients anywhere near 50 m^2/kg could be obtained, if a sheet with greatly reduced strength could somehow be prepared. Furthermore, as discussed in the introduction, the fact that the L0-L3 series of APPI sheets show a range of S_0 values between 42.0 and 28.6 m^2/kg also indicate the severe problems with this extrapolation. The only difference between these sheets is that the fibres have been cross-sectionally cut to reduce the fibre length. Even if the fibre length were halved, this would still require only one cut, on average, in each fibre and this would increase slightly the total fibre area not decrease it.

Figure 3 shows the different values of *RBA* calculated for all the data with the shape correction method for density, as given by equation 6 and the Ingmanson and Thode extrapolation. All of the shape corrected data are shown as solid points, while the data shown with the Ingmanson and Thode extrapolation method are shown as the open points. The most striking point of the two data sets is how scattered the values calculated by the extrapolation method are, whereas the shape corrected data all fall narrowly around a single straight line.

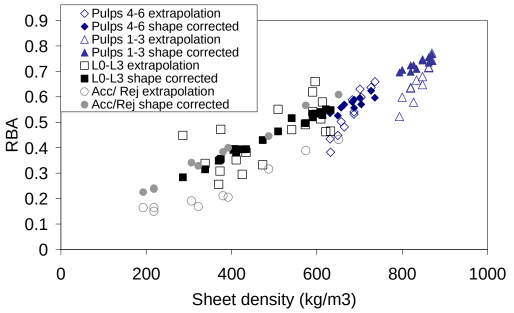

Figure 3 Comparison of RBA either by the Ingmanson-Thode extrapolation method (hollow points) or by the shape correction method for density (equation 6 with (*1-r*) =3/4) (solid points)

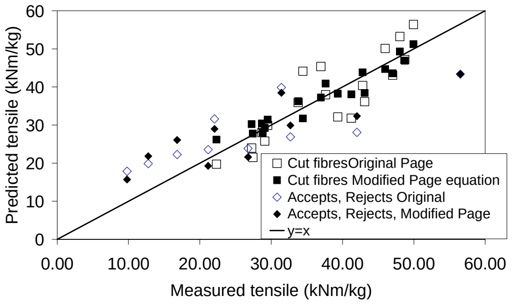

Figure 4 Tensile strength predicted from the modified (equation 8 and original (equation 5) Page equations vs. measured tensile strength for the cut fibres (L0-L3) series and the Accepts and Rejects from the APPI data

The predictions of the original and modified Page equations are shown for the APPI and ensis-Papro data in Figure 4 and Figure 5, respectively. The unknown for each of the data sets, whether using the original or the modified Page equation, was the bond strength. Therefore, for each of the data sets, the bond strength was used as a fitting parameter to minimise the sum of the squares of the difference between the measured and predicted values.

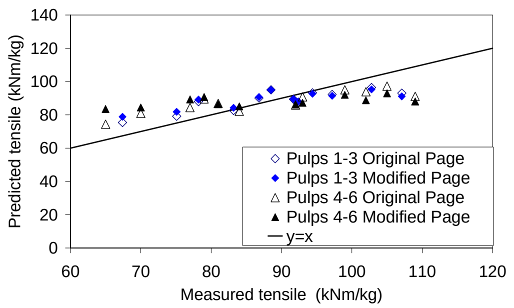

Figure 5 Tensile strength predicted from the modified (equation 8) and original (equation 5) Page equations vs. measured tensile strength for the pulps 1-6 for the ensis-Papro data

Table 4 shows the best fit bond strength for each equation and data set as well as the sum of the squares and the number of data points used in the fit. For the purposes of the fitting, the data was divided up into four groups- the cut fibres (L0-L3) for the APPI data set, the accepts and rejects for the APPI data set, pulps 1-3 for the ensis-Papro data and pulps 4-6 for the ensis-Papro data. Pulps 1-3 were grouped together because they were from different positions in the same tree. Pulps 4-6 were grouped together because they were prepared using different kraft pulping procedures from a common set of starting chips. The fibre dimension data shown in Table 1 also clearly show that these pulps divide into two groups.

Table 4 Fitted value of bond strength used to minimise sum of squares of difference between measured and fitted values

Sample	Equation	Fitted bond strength	Sum of squares (samples)
Cut fibres L0-L3	Original	1.94 MPa	533 (20)
Cut fibres L0-L3	Modified	2.69 MPa	109 (20)
Accepts/ Rejects	Original	2.03 MPa	723 (10)
Accepts/ Rejects	Modified	1.76 MPa	604 (10)
Pulps 1-3	Original	16.5 MPa	523 (12)
Pulps 1-3	Modified	21.2MPa	727 (12)
Pulps 4-6	Original	7.6 MPa	915 (12)
Pulps 4-6	Modified	10.0 MPa	1746 (12)

Figure 4 shows that both the original and modified Page equations provide reasonable fits to the APPI data, although the summary statistics of the fits show that our modified Page equation has provided a better fit to the data than the original Page equation. However, both the original and modified Page equations give poor fits to the ensis-Papro data, with the modified Page equation giving a poorer fit than the original. For the fits to the APPI data, the points are scattered around the line of 1 to 1 correspondence, while for the ensis-Papro data, it can be seen that for both data sets, the two forms of the Page equation are over-predicting strength for measured strengths ranging from 60 to 95 kNm/kg and then under-predicting for all measured strengths greater than 95 kNm/kg. The relatively poor fit for this data set is likely at least partly due to the fact that the fibre shape measurements for the ensis-Papro data were only measured on the fibres separated from the sheets that had been formed after the lowest level of refining of 500 PFI revolutions. Thus the subsequent changes in fibre wall dimensions and fibre shape produced by the PFI mill refining were not measured. Given that the fibre shape is directly incorporated into the modified Page equation through the use of the fill factor and the fibre width as variables, it would be expected then that the modified Page equation would not be accurate if these variables were changing. Another reason for the particularly poor fit is that the bond strength may be increasing as the pulp is refined.

When the bond strengths fitted for the original and modified Page equations are compared, it can be seen the fitted bond strengths are quite similar to each other for the same data set. However the fitted bond strengths average around 2 MPa for the two APPI data sets, around 9 MPa for pulps 4-6 from ensis-Papro and 18 MPa for pulps 1-3 from ensis-Papro. This is a significant issue for the useability of either the original or the modified Page equation to predict paper tensile strength. Except for pulp #4, which was commercially produced, the pulps all have more similarities than differences. The sheets were all made from laboratory produced, unbleached, never dried, radiata pine kraft pulps with similar kappa numbers of 30 (APPI pulp) and 25 (ensis-Papro pulp).

As discussed in the introduction, these fitted bond strengths cannot be directly equated to bond strengths measured directly from tensile tests on fibre-fibre joints, as the Page equation assumes that all of the bonds act collectively along the fibre and thus that each bond is equally loaded. The reality is that bonds at the fibre ends are likely to be most heavily loaded, with the loads on the bonds decreasing when moving along the fibre towards the middle. The bond strengths from the fits are thus in some unknown way that of all the bonds collectively in their average configuration. Recently, one of us has reported a new method for measuring the shear bond strength on the fibres in the sheets *(13)*. The method relies on weakening the fibres until the fibre strength is equal to the strength of one bond. The measured bond strength was 26.9 MPa, which is around 30% higher than the highest fitted bond strength used here.

The data suggest that both the original and modified Page equations should be treated with care as the equations contain the shear bond strength, which is an unknown parameter. The fact that for the experiments here, the fitted shear bond strength varied over such a large range means that the equations have little predictive power, although as Figure 4, showed, both forms of the Page equation seem capable of correctly predicting the effect on tensile strength of a change in fibre length or an increase in sheet density produced by wet pressing.

Conclusions

This paper proposes a modified form of the Page equation to take into account an improved method that the authors had previously developed to determine the relative bonded area from measurements of fibre shape and sheet density. The original and modified forms of the Page equation were tested against data from 12 different sets of sheets made from never dried, unbleached, radiata pine kraft pulps, sourced from both APPI and ensis-Papro. The bond strength was used as an unknown fitting parameter, while all the other parameters were measured. The modified Page equation gave a better fit to the APPI data, although both equations did a reasonable job of fitting the data. Both the modified and the original Page equation fitted the ensis-Papro data poorly. The best fit bond strength varied from 1.76 to 21.2 MPa. The results suggest that the Page equation has limited predictive power, since the bond strength values were so divergent.

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